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## (54) A METHOD OF TREATING EXHAUST GASES OF INTERNAL COMBUSTION ENGINES

(71) We, W. R. GRACE & CO., a Corporation organised and existing under the laws of the State of Connecticut, United States of America, of 3 Hanover Square, New York, New York 10004, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of treating exhaust gases of internal combustion engines catalytically to remove noxious gases by converting them into the less harmful entities and thereby combat pollution, in which a certain type of support material is employed for the catalyst.

Alumina, which is a common and useful support or carrier material for catalysts, is seriously affected by high temperatures. At low temperatures the alumina is in the gamma ( $\gamma$ ) or other transitional forms such as chi, kappa, eta, theta and delta. Generally these forms are all unstable at higher temperatures and are converted either directly or indirectly to the alpha ( $\alpha$ ) form. A more detailed discussion is given in "Encyclopaedia of Chemical Technology" edited by Kirk and Othmer (2nd edition, John Wiley & Sons, New York, 1963) vol. 2, pp. 48—57. The most readily obtainable of the transitional aluminas at the temperature required to make a suitable catalyst support material is gamma alumina. The transformation of the transitional alumina into alpha alumina is accompanied by loss of surface activity which in turn lessens the activity of the catalyst supported by the alumina and therefore reduces the catalysts' effectiveness. Furthermore, the alumina shrinks in volume by as much as 20% during the conversion to  $\alpha$ -alumina.

To combat pollution of the atmosphere from the exhaust gases of internal combustion engines, particularly of road vehicles, catalysts are used to convert the more noxious gases in the exhaust into less noxious chemical substances. For example hydrocarbons are oxidised to give carbon dioxide and water, carbon monoxide is oxidised to carbon dioxide and nitrogen oxides are reduced to the  $N_2$  state. These catalysts require to be supported on a mechanically strong attrition-resistant support material. The support material should be capable of withstanding temperatures as high as 1800°F. (980°C.) which are sometimes encountered in the exhausts of road vehicles.

Hitherto, alumina has not been completely satisfactory as a support material for catalyst elements for use in exhausts of internal combustion engines. The transition of gamma alumina to alpha alumina generally begins at about 1600—1800°F. (870—980°C.) and will therefore take place in the exhaust when this high temperature is reached. This transition is accompanied by shrinking and the shrinking causes attrition of the support material to take place. For example alumina balls have been known to shrink, when gamma alumina is transformed to alpha alumina, by 17% or more and when impregnated with a catalytic composition the shrinkage is as high as 22—27%. The shrinkage causes an appreciable void volume in the catalytic reactor (the part of the exhaust in which the catalyst is positioned) permitting attrition due to continuous shrinkage. Catalyst supports which shrink more than 10% are found to be unsatisfactory due to the voids created and also the loss of catalytic activity.

We have now found that, when a transitional, e.g. gamma, alumina is impregnated

with a rare earth metal oxide or a mixture of rare earth metal oxides, the alumina remains predominantly in the transitional form at 1600—1800°F. (870—980°C.) and does not undergo substantial conversion to the alpha form. This impregnated transitional alumina is especially useful for the catalysts of the conversion of noxious components of exhaust gases from internal combustion engines into less harmful entities, and it is to this aspect which the present invention is directed.

Particularly good advantage can be taken of our finding when this catalyst support material forms part of a monolith. The monolithic form is one in which the whole of the material required for a single catalyst element, i.e. usually to provide the catalyst for one exhaust, is in one piece; it is preferably cylindrical in shape. It is important that the monolith should not shrink since otherwise it will rattle within its housing and may eventually disintegrate as a result of continuous rattling vibrations.

The present invention provides a method of converting noxious components of the exhaust gas of an internal combustion engine into less harmful entities which comprises contacting the exhaust gas with a catalytic body comprising a catalytic component suitable for catalysing the conversion of noxious components of the exhaust gas of an internal combustion engine into less harmful entities, said catalytic component being supported on a monolith comprising a core of a ceramic material capable of withstanding a temperature of 1800°F. coated with a composition comprising a transitional alumina and 0.1 to 10% by weight, based on the weight of said transitional alumina, of at least one rare earth metal oxide.

The invention further includes exhaust means for an internal combustion engine, said exhaust means containing a catalytic body as defined above.

The transitional alumina will normally be gamma alumina.

The ceramic material which forms the core of the monolith may be, for example, alpha-alumina, magnesia-alumina spinel, mullite, zircon-mullite or cordierite.

The catalytic body for use as an exhaust catalyst will usually comprise 0.1—70% by weight of the catalytic component and 30—99.8% by weight (i.e. substantially the remainder) of the monolith.

Rare earth metal oxides which are useful in the invention include the oxides of scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium. A mixture of two or more of these oxides may be employed.

The monolith may be prepared by a process which comprises coating a core of a

ceramic material capable of withstanding a temperature of 1800°F (980°C) with an aqueous slurry containing a transitional alumina and drying the coated core to remove the water of the slurry, rare earth metal salt(s) decomposable on heating to the oxide(s) either (a) being present in the slurry or (b) being composited with the dried coated core by impregnation from solution of the rare earth metal salt(s) followed by removal of solvent (normally water) of said solution, e.g. by drying, from the thus impregnated coated core, the coated core containing the rare earth metal salt(s) being heated, at some stage during the process, at a temperature at which the rare earth metal salt(s) decompose(s) to the oxide(s).

Ordinarily it is desirable thereafter to calcine the dried coated core at a temperature below that at which the transitional alumina would be predominantly converted to alpha alumina. The rare earth metal salt will usually be one which decomposes to the oxide in the drying step, but in principle it may be one which decomposes on heating at any temperature below the calcination temperature.

A particularly useful method of preparing the starting ceramic core is that disclosed in our British Patent Application No. 49203/71 (Serial No. 1,349,400). In this method a polyolefin, plasticiser, and filler (preferably alumina) are mixed, the mixture is shaped, the plasticiser is extracted, the polyolefin is burned-off, and the resulting filler is sintered, leaving a monolithic structure.

The core is preferably of alpha-alumina.

In one embodiment of the above-described process of preparing the monolith, the core is coated with a thin layer of pre-prepared gamma alumina which after its preparation has itself been impregnated with rare earth metal salt(s). The following is one illustrative procedure for this impregnation. Gamma alumina particles are placed in a container and preferably rotated to permit a uniform impregnation with a rare earth metal salt solution (having a concentration of 0.1 to 40%, preferably 0.1 to 10%, by weight of rare earth metal expressed as rare earth metal oxide); sufficient rare earth metal salt solution is added to fill the pores of the alumina.

The following is a detailed description of another method of coating the core to prepare the monolith. The core is immersed in a homogeneous slurry prepared by mixing alumina trihydrate (average particle size about 0.2 micron) with a 2/3% solution of carbomethyl cellulose (CMC) in a weight ratio of about 1:2. The slurry also contains sufficient rare earth metal, preferably in the form of a salt dissolved in the water of the slurry, such that the finally obtained particulate gamma alumina contains about 0.1—10% by weight rare earth metal oxide. The CMC has the effect of quickening the drying steps which

are to follow. After the core has been dipped into the slurry, excess slurry is shaken off and the treated core is sprayed with an air hose to remove excess slurry from within the core.

- 5 The whole is dried at 150—200°F (65—95°C) for one 1/2 hour, 1 hour at 300°F (150°C) and then at least one hour more at a temperature of about 1050°F (565°C) to convert the alumina trihydrate to gamma alumina. This procedure provides a monolith containing 10—12% by weight stabilised gamma alumina, said gamma alumina being impregnated with 0.1—10% by weight, based on the weight of the alumina, of rare earth metal oxide.

15 In another embodiment, the particulate gamma alumina does not contain a rare earth metal salt and after the core has been coated with this particulate gamma alumina, it is sprayed with or immersed in a rare earth metal salt solution.

20 The rare earth metal-stabilised gamma alumina coating is then impregnated with a catalytic component useful in purifying internal combustion engine exhaust emissions. Some compositions useful as this catalytic component are disclosed in United States Patent Nos. 3,288,558; 3,295,918; 3,304,150; 3,322,491; 3,338,666; 3,346,328; 3,455,843 and 3,470,105. (The term "catalytic component" is used herein to refer collectively to the active catalytic ingredients, in distinction from the ceramic materials, and includes a single substance or a mixture of two or more substances). Preferably, the catalytic component comprises (includes or consists essentially of): (i) copper, chromium and manganese oxides; (ii) copper, chromium and manganese oxides and also palladium; or (iii) cobalt, copper, manganese and iron oxides. Below are listed examples of catalytic components, designed A, B, C and D, giving percentages of ingredients reckoned by weight of the total catalytic body inclusive of the support:

- A: 10% CuO, 4.0% Cr<sub>2</sub>O<sub>3</sub>, 0.02% Pd  
 B: 8% CuO, 12.0% MnO<sub>2</sub>, 0.02% Pd  
 C: 4% CuO, 6% MnO<sub>2</sub>, 4% Cr<sub>2</sub>O<sub>3</sub>, 0.02% Pd  
 50 D: 4% CuO, 6% MnO<sub>2</sub>, 6% Cr<sub>2</sub>O<sub>3</sub>.

Of course, other catalytic components such as platinum are useful as an alternative to the above compositions.

55 A particularly suitable method of impregnating these catalytic components onto the stabilised gamma alumina is that described in United States Patent No. 3,455,843 wherein material comprising component (A) is prepared by impregnating gamma alumina with a copper-palladium salt solution followed by vacuum impregnation with chromia (Cr<sub>2</sub>O<sub>3</sub>). Material comprising component (B) may be prepared by immersing gamma alumina in a

copper-manganese-palladium salt solution, when this is followed by vacuum impregnation with chromia, stabilised gamma alumina containing component (C) is obtained. Component (D) is similarly prepared.

The following Examples further illustrate the invention. "—325 mesh" means smaller than the U.S. Standard Sieve No. 325 apertures which are 44 microns in diameter. In order to evaluate the amount of shrinkage which occurs, the catalytic support is subjected to a temperature of about 1800°F (980°C) for 24 hours. This is referred to as the "shrinkage endurance test."

Examples 1—20 do not describe monoliths but are included for reference because they demonstrate the effects of the incorporation of the rare earth metal in the transitional alumina. Examples 21—28 describe the preparation of monoliths.

#### EXAMPLE 1

85 100 grams of balls of gamma alumina were placed in a container and rotated. A rare earth metal chloride solution having a rare earth metal concentration of 7% weight/weight calculated as oxides and having an analysis by weight in terms of oxides of about 55.3% La<sub>2</sub>O<sub>3</sub>, 20.0% Ce<sub>2</sub>O<sub>3</sub>, 17.3% Nd<sub>2</sub>O<sub>3</sub>, 6.02% Pr<sub>2</sub>O<sub>3</sub> and 1.33% Sm<sub>2</sub>O<sub>3</sub> was added until the pores of the alumina balls were filled. 90 ml. of solution were required, thus impregnating the alumina with 6% of rare earth metal oxide, based on the weight of the alumina. The alumina balls thus uniformly impregnated were removed from the container, allowed to dry at about 110°C. for 2 hours, heated at 1800°F. (980°C.) for 5 hours and allowed to cool to room temperature. Upon cooling, it was observed that a shrinkage of only 3% from the original volume had occurred and that the alumina had remained in the gamma form.

After being subjected to the "shrinkage" endurance test" described above the stabilised alumina balls showed a total volume shrinkage of only an additional 5% (making a total of about 8%).

#### EXAMPLES 2—4

Example 1 was repeated except that the concentration of the rare earth metal chloride solution was varied. The results are shown below.

Example No.	Weight % Rare Earth Metal Oxide	Percent Shrinkage	
2	0	17	
3	2	12	
4	4	9	120

As can be seen, the use of the rare earth metal oxide drastically reduced shrinkage relative to that of the untreated alumina.

#### EXAMPLES 5—17

Example 1 was repeated, with similar re- 125

sults, except that the following rare earth metal chlorides and rare earth metal chloride mixtures were used, percentages being by weight and reckoned as oxides of the rare earth metals.

#### Example

No.	Rare Earth Metals
5	lanthanum
6	cerium
10	praseodymium
8	neodymium
9	cerium (60%) and neodymium (40%)
10	cerium (80%) and samarium (20%)
15	cerium (50%) and lanthanum (50%)
12	cerium (70%), praseodymium (25%), samarium (5%)
20	cerium (80%), praseodymium (10%), neodymium (10%)
14	lanthanum (80%), samarium (10%), neodymium (10%)
15	lanthanum (60%), praseodymium (10%), cerium (30%)
25	lanthanum (80%), praseodymium (10%), neodymium (8%), samarium (2%)
17	lanthanum (25%), praseodymium (2%), neodymium (4%), samarium (1%), cerium (68%).

#### EXAMPLE 18

An automobile exhaust catalyst containing by weight 4% CuO, 6% Cr<sub>2</sub>O and 4% MnO<sub>2</sub> was prepared by impregnating 100 grams of stabilised gamma alumina balls prepared in Example 1 with a solution prepared by dissolving 14.48 grams of Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O,

9.40 grams of CrO<sub>3</sub> and 9.64 grams of Mn(NO<sub>3</sub>)<sub>2</sub> in 85 ml. of water. This material was dried at 150°C. for 2 hours and then treated with 75 ml. of a palladium tetramine nitrate solution containing 0.023 g. palladium. The impregnated stabilised gamma alumina was then dried at 150°C. for 2 hours and calcined at 1400°F. (760°C.) for 3 hours. The total volume shrinkage of this catalyst after the "shrinkage endurance test" was 6%. This catalyst was labelled "Catalyst 1".

#### EXAMPLE 19

An automobile exhaust catalyst was prepared as in Example 18 except that the gamma alumina had not been stabilised with a rare earth metal oxide. This catalyst had a shrinkage of 22% after the "shrinkage endurance test" and was labelled "Catalyst 2".

#### EXAMPLE 20

This Example illustrates the enhanced catalytic activity of the rare earth metal stabilised automobile exhaust catalyst ("Catalyst 1") when compared with the catalytic activity of the non-rare earth metal stabilised catalyst ("Catalyst 2").

The activity of the catalysts was determined by passing a simulated exhaust gas composition consisting of: 250 ppm C<sub>3</sub>H<sub>8</sub>, 1000 ppm NO, 1.0% CO, 10% CO<sub>2</sub>, 10% H<sub>2</sub>O, 2.0% O<sub>2</sub> and the balance N<sub>2</sub> through a fixed bed catalytic converter at a gaseous hourly space velocity of 14,000 volumes of gas per volume of catalyst per hour and recording the temperature at which a certain percentage (denoted in Table 1) of CO and C<sub>3</sub>H<sub>8</sub> had been converted to CO<sub>2</sub> and H<sub>2</sub>O.

The results for "Catalyst 2" (the non-stabilised alumina) and "Catalyst 1" (the rare earth metal-stabilised alumina) are given in Table I.

TABLE I

Catalyst No.	Exhaust gas components	Temperatures in °F. (°C.) for Conversion (mole percent) of			
		10%	50%	90%	
85	1	CO	341(172)	464(240)	652(344)
	2	CO	379(193)	504(262)	620(327)
	1	C <sub>3</sub> H <sub>8</sub>	422(217)	569(298)	754(401)
	2	C <sub>3</sub> H <sub>8</sub>	429(221)	545(285)	682(361)

As can be seen, the minimum temperatures at which the catalysts are effective are very similar. Of course, the catalysts are in practice submitted to very much higher temperatures, e.g. 1800°F. (980°C.), and the attrition-resistance of Catalyst 1 at such temperatures is greater than that of Catalyst 2 as demonstrated by the shrinkage endurance test, the shrinkage of Catalyst 1 being about a quarter of that of Catalyst 2.

#### EXAMPLE 21

A cylindrical honeycombed porous ceramic monolithic core of alpha alumina was prepared as described in Example 1 of our British Patent Application No. 49203/71 (Serial No. 1,349,400). The monolithic core was then dipped into a slurry made by mixing 250 grams of rare earth metal-stabilised gamma alumina prepared following the procedure of Example 1 and 510 g of a 2/3 weight percent

5 solution of carboxymethyl cellulose (CMC) in water (to decrease the drying time). The core was then removed from the slurry, shaken to remove excess slurry, and subjected to a stream of compressed air to remove excess slurry within the structure. The coated core was then dried for 1/2 hour at 150—200°F. (65—95°C.), 1 hour at about 300°F. (150°C.) and then 4 hours at 1600°F. (870°C.) to calcine the stabilised gamma alumina. The resulting monolith contained about 10% by weight coating, based on the total weight of the structure.

10 This monolith was then impregnated with 6%  $\text{Cr}_2\text{O}_3$ , 4%  $\text{MnO}_2$  and 4%  $\text{CuO}$  (by weight) by immersing the monolith for 2 hours in a solution containing 14.48 grams  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 9.40 grams  $\text{CrO}_3$  and 9.64 grams  $\text{Mn}(\text{NO}_3)_2$  in 130 ml. of water. The monolith was dried for 2 hours at 150°C. and calcined at 1400°F. (760°C.) for 3 hours.

#### EXAMPLE 22

25 Example 21 was repeated except that the monolith was impregnated with 0.2% by weight platinum by immersing for 2 hours in a solution of platinum tetramine nitrate containing 0.2 g. Pt in 85 ml. of water. The monolith was dried for 2 hours at 150°C. and calcined at 1400°F. (760°C.) for 3 hours.

#### EXAMPLES 23—28

30 Example 21 was repeated except that the following materials were used instead of alpha alumina in the preparation of the monolithic core:

35 Example 23: a mullite composition of 75% by weight raw kyanite (—325 mesh,  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ) and 25% by weight South Carolina kaolin (commercially available from Huber Corporation);

40 Example 24: a mullite composition of 75% by weight calcined mullite (—325 mesh, a 70% alumina bauxite-clay calcine) and 25% by weight South Carolina kaolin (Huber Corporation);

45 Example 25: a mullite composition of 85% by weight calcined mullite (—325 mesh, a 70% alumina bauxite-clay calcine) and 15% by weight Jackson ball clay (commercially available from Kentucky Tenn. Clay Corp.);

50 Example 26: a zircon-mullite composition of 50% by weight calcined mullite (—325 mesh, a 70% alumina bauxite-clay calcine), 25% by weight ground zircon (—325 mesh) and 25% by weight South Carolina kaolin;

55 Example 27: a spinel prepared by decomposing high purity magnesium aluminate; and

60 Example 28: a cordierite composition prepared by mixing 50% by weight Florida kaolin and 50% by weight sierralite (a relatively pure prochlorite commercially available from United Sierra Div., Cyprus Mines Corp.).

In each Example there was little or no volume shrinkage of the product.

#### WHAT WE CLAIM IS:—

65 1. A method of converting noxious components of the exhaust gas of an internal combustion engine into less harmful entities which comprises contacting the exhaust gas with a catalytic body comprising a catalytic component suitable for catalysing the conversion of noxious components of the exhaust gas of an internal combustion engine into less harmful entities, said catalytic component being supported on a monolith comprising a core of a ceramic material capable of withstanding a temperature of 1800°F. coated with a composition comprising a transitional alumina and 0.1 to 10% by weight, based on the weight of said transitional alumina, of at least one rare earth metal oxide.

2. A method according to claim 1 wherein the rare earth metal oxide comprises a cerium oxide.

3. A method according to claim 2 wherein the rare earth metal oxide is a mixture consisting essentially of cerium, lanthanum, neodymium, praseodymium and samarium oxides.

4. A method according to claim 2 or 3 wherein the cerium oxide is cerium (IV) oxide.

5. A method according to claim 1 wherein the rare earth metal oxide is selected from scandium, yttrium, lanthanum, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium oxides and mixtures of two or more of such oxides.

6. A method according to any preceding claim wherein the transitional alumina comprises gamma alumina.

7. A method according to any preceding claim wherein the core is of alpha-alumina, magnesia-alumina spinel, mullite, zircon-mullite or cordierite.

8. A method according to any preceding claim wherein the core has been obtained by a process claimed in our British Patent Application No. 49203/71 (Serial No. 1,349,400).

9. A method according to any preceding claim wherein the monolith has an overall substantially cylindrical shape.

10. A method according to any preceding claim wherein the monolith has been prepared by a process which comprises coating a core of a ceramic material capable of withstanding a temperature of 1800°F with an aqueous slurry containing a transitional alumina and drying the coated core to remove the water of the slurry, rare earth metal salt(s) decomposable on heating to the oxide(s) either (a) being present in the slurry or (b) being composited with the dried coated core by impregnation from solution of the rare earth metal salt(s) followed by removal of solvent of said

- solution from the thus impregnated coated core, the coated core containing the rare earth metal salt(s) being heated, at some stage during the process, at a temperature at which the rare earth metal salt(s) decompose(s) to the oxide(s).
- 5 11. A method according to claim 10 wherein the dried coated core is calcined at a temperature below that required predominantly to convert the transitional alumina to alpha alumina.
- 10 12. A method according to claim 1 wherein the monolith has been prepared by a process substantially as described in any one of Examples 21—28.
- 15 13. A method according to any preceding claim wherein the catalytic component comprises copper oxide, chromium oxide and palladium.
- 20 14. A method according to claim 13 wherein the catalytic component further comprises manganese oxide.
15. A method according to any one of claims 1—12 wherein the catalytic component comprises cobalt oxide, copper oxide, manganese, oxide and iron oxide.
- 25 16. A method according to any one of claims 1—12 wherein the catalytic component consists essentially of platinum.
- 30 17. Exhaust means for an internal combustion engine, said exhaust means containing a catalytic body defined in any preceding claim.

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